

AD-A173 649

MOLECULAR ELECTRONICS FOR FREQUENCY DOMAIN OPTICAL
STORAGE PERSISTENT SPE. (U) IBM RESEARCH LAB SAN JOSE
CA W E MOERNER 25 MAR 85 RJ-4648 (49636)

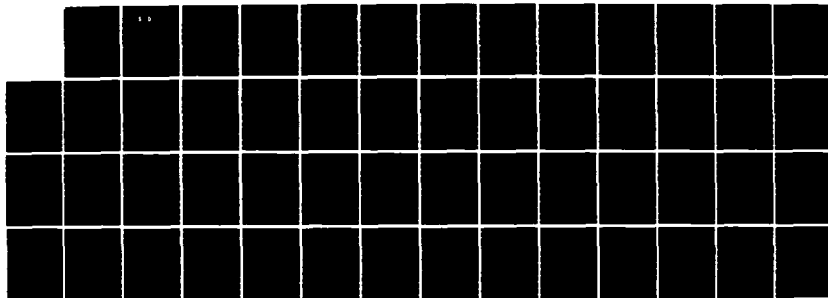
1/1

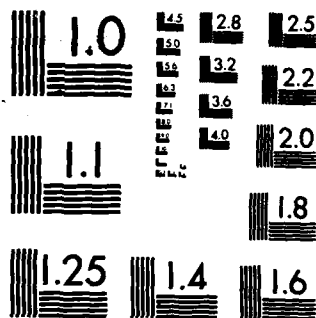
UNCLASSIFIED

N00014-84-C-0700

F/G 9/3

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A173 649

12

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE OCT 20 1985			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #1, IBM RJ 4648			7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Chemistry Division, Code 1113		
6a. NAME OF PERFORMING ORGANIZATION IBM Almaden Research Center			7b. ADDRESS (City, State, and ZIP Code) Burlington, VA 22217		
6c. ADDRESS (City, State, and ZIP Code) 650 Harry Road San Jose, CA 95120-6099			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-C-0708		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)		10. SOURCE OF FUNDING NUMBERS	
				PROGRAM ELEMENT NO.	PROJECT NO.
				TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Molecular Electronics for Frequency Domain Optical Storage: Persistent Spectral Hole-Burning - A Review					
12. PERSONAL AUTHOR(S) W. E. Moerner					
13a. TYPE OF REPORT Interim Technical		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Year, Month, Day) March 25, 1985	
15. PAGE COUNT 49					
16. SUPPLEMENTARY NOTATION Journal of Molecular Electronics					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Molecular electronics, spectral hole-burning, frequency domain optical storage, solid state photo chemistry, photon gating.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Persistent spectral hole-burning (PHB) is a phenomenon that allows an additional dimension, the frequency at which spectral holes are written, to be used to encode digital data. PHB can be used to store a large number of bits of information in the volume irradiated by a focused laser beam, leading to a possible future storage technology, frequency domain optical storage. A large number of photochemical and photophysical mechanisms have led to the production of spectral holes; a wealth of information has been learned about host-guest interactions, dephasing, and solid-state photochemistry at low temperatures. The general structure of a frequency domain optical store places a set of constraints on the engineering of such a system as well as on the materials used as recording media. The dynamics of the hole-burning process are crucial; for monophotonic mechanisms in particular, a set of stringent constraints can be derived that limit the applicability of this class of materials. Recent discoveries of two-color, photon-gated hole-burning offer special promise for nondestructive reading and improved performance; much basic research remains to be done in this new class of photochemical hole-burning mechanisms in order to find appropriate materials for frequency domain optical storage.					
DTIC FILE COPY					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED / UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-84-C-0708

R&T Code 413a001---01

Technical Report No. 1

Molecular Electronics for Frequency Domain Optical Storage:
Persistent Spectral Hole-Burning - A Review

by

W. E. Moerner

Prepared for Publication

in the

Journal of Molecular Electronics

IBM Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

March 25, 1985

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

* This document has been approved for public release and sale; its distribution is unlimited.

RJ 4648 (49656) 3/25/85
Physics

**MOLECULAR ELECTRONICS FOR FREQUENCY DOMAIN OPTICAL STORAGE:
PERSISTENT SPECTRAL HOLE-BURNING**

W. E. Moerner

IBM Research Laboratory
San Jose, California 95193

ABSTRACT: Persistent spectral hole-burning (PHB) is a phenomenon that allows an additional dimension, the frequency at which spectral holes are written, to be used to encode digital data. PHB can be used to store a large number of bits of information in the volume irradiated by a focused laser beam, leading to a possible future storage technology, frequency domain optical storage. A large number of photochemical and photophysical mechanisms have led to the production of spectral holes, and a wealth of information has been learned about host-guest interactions, dephasing, and solid-state photochemistry at low temperatures. The general structure of a frequency domain optical store places a set of constraints on the engineering of such a system as well as on the materials used as recording media. The dynamics of the hole-burning process are crucial; for monophotonic mechanisms in particular, a set of stringent constraints can be derived that limit the applicability of this class of materials. Recent discoveries of two-color, photon-gated hole-burning offer special promise for nondestructive reading and improved performance; much basic research remains to be done in this new class of photochemical hole-burning mechanisms in order to find appropriate materials for frequency domain optical storage.

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



I. Introduction

Conventional optical storage (for example, compact audio disk technology) consists of focusing a laser beam to a diffraction-limited spot near $1\text{ }\mu\text{m}$ in diameter in a recording material and writing a single bit of information into the volume irradiated by the laser by ablative, magneto-optic, or other means [1]. The phenomenon of persistent spectral hole-burning (PHB, also called photochemical hole-burning although photophysical hole-burning also occurs) has the interesting property of allowing as many as 1000 or more bits of information to be stored in the volume irradiated by a single focused laser beam. PHB utilizes an additional dimension beyond x-y spatial dimensions to achieve this dramatic increase in areal storage density. In effect, various bits are addressed by the laser frequency or wavelength at which they are stored, hence the name "frequency domain optical storage" [2] [4] [3] [5] is used to mean the use of PHB for optical storage of digital data. PHB is a photoinduced process that occurs for certain absorbing centers in solid matrices at low temperatures, and this article is devoted to a description of PHB mechanisms and dynamics as they apply to frequency domain optical storage. Of course, the feasibility of such a data storage scheme depends critically upon having recording materials that undergo spectral hole-burning with certain well-defined characteristics. It is a stimulating and interdisciplinary challenge for the solid-state spectroscopist, photochemist, and laser physicist to find suitable materials and to devise detection techniques that make this application of molecular electronics possible.

To achieve spectral hole-burning, molecules (or other absorbing centers such as color centers or ions) must be dispersed in a suitable transparent matrix and cooled to liquid helium temperatures. (In this article, we refer to the generic absorbing center as a "molecule" for

convenience wherever possible.) The molecules must be sufficiently rigid and sufficiently uncoupled from the host lattice that the lowest energy optical absorption is predominantly a "zero-phonon" absorption, i. e., a purely electronic or vibrational transition with small Franck-Condon distortion. Further, the concentration of the molecules in the ideal case should be low enough so that the various molecules can be regarded as isolated. If the host matrix were a perfect crystal as in the upper half of Figure 1, all the molecules would have identical environments and therefore identical absorption frequencies. The absorption line would then be a single narrow line with width equal to the homogeneous width of the transition, Γ_H .

In a real crystal, glass, or polymer, unavoidable local strains due to vacancies, dislocations, other defects, or the randomness of the host itself cause the various molecules in the solid to have slightly different local environments. In this case (see the lower half of Figure 1), the way in which the sample absorbs light in the lowest energy absorption can be viewed as a superposition of narrow homogeneous absorption profiles with a distribution of center frequencies. The result is a broad, smooth absorption line of width Γ_I that is said to be inhomogeneously broadened. It is the fact that the local environments of the various molecules are different that makes the various molecules absorb slightly different laser frequencies, even though the same electronic transition is being probed. Thus, the first requirement for the formation of a persistent spectral hole is an inhomogeneously broadened absorption line.

Referring now to Figure 2(a), if a laser beam with a well-defined wavelength or frequency irradiates such an inhomogeneously broadened absorption line, only those molecules that are in resonance with the laser can be excited. If the laser linewidth is less than Γ_I or better yet less than Γ_H as is usually the case, one can selectively excite different classes or groups of

molecules simply by tuning the laser. The number of different classes of molecules that can be accessed in this way is on the order of the ratio of the inhomogeneous width to the homogeneous width, Γ_I/Γ_H , a factor which can range from 10 to 10^4 . (It is precisely because we want this factor to be large that liquid helium temperatures are required. At higher temperatures, Γ_H becomes larger than Γ_I due to phonon broadening effects.) If the laser is focused to a small spot, the size of that spot is limited by the wavelength of the light itself to be larger than roughly one micron in diameter for visible or near ir irradiation. Even within the small volume irradiated by a micron-sized laser beam, a narrowband tunable laser can probe different groups of molecules simply by changing the laser wavelength.

Now if the molecules undergo a photo-induced change when light is absorbed (see Figure 2(b)) such that the product does not absorb at the laser frequency ω_1 , the optical absorption at ω_1 decreases. Such light-induced changes may involve a photochemical change in the molecule itself where a product is formed [6] [7], a light-induced change in the local environment near the molecule[8], or a reorientation of the molecule itself[9], to name a few possible mechanisms. In general, the product will interact differently with the local environment than the educt; hence the product absorption will in general be inhomogeneously broadened once more, even though the educt centers giving rise to the product formed a homogeneous packet. The resulting decrease or "dip" at ω_1 in the absorption line is called a spectral hole. In practice, the laser emission linewidth is usually less than Γ_H ; in this case the hole width (full width at half-maximum, FWHM) is $2 \Gamma_H$. The laser can then be tuned to another frequency, ω_2 , and a different group of molecules in the focal volume will be selected for burning. Thus, the second requirement for PHB is a photoinduced change in the molecule such that the absorption decreases at the exciting laser wavelength.

We are particularly interested in this article in materials in which the photoinduced change persists on time scales of months or years at low temperatures. In this case, the spectral holes at various locations within the line can be used to encode binary information, where, for instance, the presence of a hole at a particular frequency within the inhomogeneous line might correspond to a binary "1" and the absence of a hole might correspond to a binary "0". Since in one laser spot many groups of molecules are available, 1000 or perhaps 10,000 bits can, in principle, be stored in the frequency domain in the volume illuminated by a focused laser beam, resulting in potential areal storage densities as large as 10^{11} - 10^{12} bits/cm². Because the frequencies at which holes are burned adds a new dimension for addressing, this type of data storage scheme is called frequency domain optical storage.

To illustrate a particular hole-burning mechanism for the convenience of the reader, consider the free-base phthalocyanine molecule, H₂Pc, shown in Figure 3. This molecule has been studied in detail in a number of studies [5] [6] [7] ; here only the general features will be described. Due to the extensive conjugation and ring-like structure, H₂Pc is fairly rigid and planar and hence would be expected to have an essentially "zero-phonon" (and zero-libron) origin absorption. The molecule exists in two tautomeric forms in which the two central protons are bonded either horizontally as shown or vertically. These two tautomers are equivalent in free space, but in a host matrix with local anisotropy and strains the two tautomers absorb at wavelengths that might differ by as much as 30 - 50 cm⁻¹. When light is absorbed by the 0-0 singlet transition of one tautomer, there is a certain probability that the molecule will tautomerize into the other tautomeric form. When this occurs, the absorption at the exciting wavelength will decrease, leaving a spectral hole. The molecules can, in principle, be transformed back and forth between the two tautomers at will, simply by

irradiating the tautomer absorptions appropriately. (The molecule can also be converted between the two tautomeric forms with heat.)

As a further illustration, Figure 4 shows the inhomogeneously broadened origin absorption for H_2Pc in poly(methyl methacrylate) (PMMA) at 1.4K. In this amorphous host, the inhomogeneous broadening is so strong that the splitting due to the two tautomers for a given site is completely obscured by the distribution of sites. This does not effect the basic process, however, it only means that the product absorption appears as increased absorption somewhere within the inhomogeneous lineshape. Several photochemical holes have been burned in the line near 6950 Å, and a portion of the spectrum is shown on an expanded scale in Figure 5. These holes can be decoded into a sequence of "1's" and "0's" as shown at the bottom of the figure. It is to be emphasized that this structure in the absorption line is not due to any resonances or specific energy level structure: the holes were formed at only those wavelengths that were exposed to fixed wavelength laser radiation.

It is to be emphasized that even though the frequency domain optical storage concept sounds simple, this idea cannot be regarded as a fully practical technology at the present time. Indeed, no single material exists that displays all the characteristics required for reliable digital data storage, and that is why basic physics and chemistry research is ongoing in this area. In the rest of this article, several critical materials issues and their partial solutions will be described. In Section II, the various mechanisms that have given rise to photochemical hole-burning or photophysical hole-burning will be summarized, in order to illustrate the wide variety of mechanisms that can lead to hole-burning. Then, in Section III, the materials and systems requirements that are critical for frequency domain optical storage applications will be presented. The research efforts over the past three years to meet several of these

requirements will be outlined. In Section IV, the particular constraints that exist for single photon mechanisms will be presented, and an optimization of materials parameters will be completed. Gated or two-step PHB offers new promise for improved reading properties and in Section V, several general classes of gated systems as well as two recent discoveries will be presented.

II. Survey of Materials Showing Persistent Spectral Hole-Burning

Microscopic mechanisms leading to PHB can be roughly classified into two categories: photochemical and nonphotochemical (or photophysical). In general, photochemical mechanisms involve some change in the absorbing center itself, such as bond breaking, ionization, isomerization, tautomerization, etc. Nonphotochemical mechanisms arise from a change in the environment around the center, or a reorientation of the center itself. Although this classification is not completely rigorous, it does provide a good starting point for discussion of mechanisms. In this section, a variety of systems undergoing PHB will be described briefly, and the reader is urged to consult the references for further detail.

Table 1 provides a partial list of materials exhibiting persistent spectral hole-burning. This list is not all-inclusive; rather, examples have been selected from the literature to illustrate the broad range of mechanisms that can lead to PHB. Starting at the top of the table, free-base phthalocyanine molecules in n-alkanes and polymers were among the first systems to show persistent hole-burning effects[10]. The mechanism is proton tautomerization as described in the introduction, and extensive research has been performed on dephasing and temperature dependence of the hole widths [5] [6] [7] as well as a variety of other properties, such as

pressure-induced spectral diffusion[11] and hole-burning bottlenecks [12]. In fact, holes have been burned in 100 ns in this system [13], and this work will be described in more detail below. Free-base porphyrins and chlorin also undergo hole-burning via tautomerization of the central protons [14]. Research has concentrated on homogenous linewidths in a variety of hosts [15], tautomeric site distributions [16] [17] , dephasing measurements to 0.3K in amorphous hosts [18], and Stark effects [19].

Aggregate color centers in inorganic crystals form another interesting class of materials for PHB[20], because these systems have strong zero-phonon lines in the visible or near infrared. The basic mechanism is thought to involve photoinduced tunnelling of an electron away from the color center to a nearby trap. This dramatically changes the character and energy levels of the color center, yielding a drop in absorption at the excitation wavelength. After the first observation of PHB for F_3^+ centers in NaF[21], PHB was observed in the technologically important GaAlAs laser wavelength region near 8300 Å for R' centers in LiF[22]. A variety of other centers have been investigated for low temperature hole widths, dephasing, polarization properties, etc. including the 6070 Å center in NaF [23], various centers in diamond [24] , a very high efficiency center in NaF-OH⁻ at 8892 Å[25], and color centers in thin films[26].

Electrons can also be trapped at electrophilic sites in organic glasses. In one early experiment, tetra-methyl-p-phenylenediamine (TMPD) molecules in 3-methylpentane or methyltetrahydrofuran were photoionized to yield a broad inhomogeneously broadened trapped electron spectrum near 1.8 μm. Irradiation with a laser produced spectral holes, presumably by photoionization of the electron traps[27].

1,4-dihydroxy-anthraquinone(quinizarin) in hosts such as alcoholic glasses or boric acid glass has been observed to undergo PHB via rearrangements of the hydrogen bonds. Several reviews have thoroughly described the various research efforts to understand the low temperature photochemistry of this system [5] [7] [28] . To mention a few, studies have considered the proton transfer process[29], electron-phonon coupling and hole lineshapes[30], host TLS dynamics [31], hole recovery rates [32] , and quantum efficiency[33].

A totally different photochemical change occurs when hole-burning is performed for s-tetrazine and dimethyl-s-tetrazine in crystals and polymers. The molecule undergoes irreversible photodecomposition, and in some hosts, I^2 power laws are observed indicating a possible two-photon mechanism [28] [34] [35] [36] . In poly(vinyl carbazole), nonphotochemical hole-burning has been reported in addition to photochemical hole-burning [37].

Recently, a new mechanism for photochemical hole production in inorganic hosts has been observed: photoionization of divalent rare earth ions in alkaline earth fluoride crystals [38] [39] . This opens up a new class of materials for PHB and more examples of this process are expected in the near future.

As a final example of photochemical processes for hole production, conformer interconversion has been observed for 1,2-difluoroethane and related molecules in rare gas matrices [40] [41] [42] . Using CO_2 or lead salt diode lasers, molecules were transformed between trans and gauche conformations, yielding spectral holes. Because the molecular changes in this case are fairly subtle compared to photodissociation or photoionization, it may be debated whether this process should be regarded as photochemical or nonphotochemical.

We now consider those mechanisms for PHB listed in the second half of Table 1 that do not result in an intrinsic alteration of the absorbing center itself, called nonphotochemical or photophysical mechanisms. In most cases, the product absorption for nonphotochemical processes is not very far removed in frequency space from the original educt absorption. In fact, in some materials the product absorption appears as regions of increased absorption immediately adjacent to the hole[9]. In addition, the energy barriers preventing reverse reactions may not be very high, so that nonphotochemical holes often irreversibly disappear upon warming above liquid helium temperatures. These properties make nonphotochemical mechanisms somewhat less useful for storage applications than photochemical processes, but individual materials may violate this general trend.

Electronic transitions of photostable molecules in glasses and polymers form the largest class of materials for nonphotochemical hole-burning. The basic process here involves excitation of the molecule, transfer of energy to the surrounding amorphous environment, and stimulation of transitions among the two-level systems (TLS's) of the host which then alters the absorption energy of the molecule [8]. The effect appears to be quite general, and has been studied for tetracene in glasses [43] [44] , perylene in glasses and polymers [45] [46] , resorufin in polymers [47] [33] , and dye molecules in polymers[48], to give a partial list. For certain hosts, the vibronic structure within the inhomogeneous line can be conveniently probed using nonphotochemical hole-burning techniques[48].

A similar mechanism exists for photophysical hole-burning for ions in glasses and polymers. Here again the absorbing center itself undergoes no intrinsic change, and transitions among the TLS's of the amorphous matrix or rearrangements of the nearby host structure are responsible for the hole formation. The effect has been observed for Eu^{+3} , Pr^{+3} , and Nd^{+3}

in silicate glasses [49] [50] [51] and even for Pr^{+3} in polymer films[52]. These holes can persist for times much longer than the spin-lattice relaxation times because the relevant back reaction involves TLS tunnelling times of the nearby host (min to hours or longer).

What about photostable guest molecules in crystalline host matrices? For the case of hydrogen bonded crystals such as benzoic acid, nonphotochemical hole-burning can easily be observed. In particular studies have been performed for pentacene in benzoic acid crystals [53] [54] as well as for thioindigo in benzoic acid [55].

An interesting question is whether or not photophysical hole-burning can occur for stable absorbing centers in rigid, crystalline hosts such as alkali halides. For the case of tetrahedral ReO_4^- ions in alkali halides, hole-burning does occur due to light-induced reorientations of the molecule in the host [9] [56] . For certain choices of double dopant, antihole are also observed for this interesting system[57]. In recent measurements, hole-burning has also been observed for CN^- in alkali halide hosts as well, with molecular reorientation as a suspected mechanism[58].

As a final example of nonphotochemical PHB, trivalent rare earth ions in crystals have shown PHB due to optical pumping among nuclear hyperfine and quadrupole levels [59] [60] [61] [62] . Elegant spectroscopic studies of nuclear and electronic Zeeman effects as well as optically detected NMR have been performed, and homogeneous widths as small as 750 Hz have been observed [63]. The holes in these systems persist for times on the order of the spin-lattice relaxation time, which may be seconds or minutes. This makes these materials less attractive for data storage applications, but we include them here for completeness.

To conclude this brief summary of classes of materials that show PHB, we may only remark that even though wide variety of mechanisms and host-guest combinations have been studied, much remains to be done. Hole formation is a fairly general process for zero-phonon excitations in solids at low temperatures, and gives information about multiple stable ground states of the coupled host-guest system that may not be observable at elevated temperatures. Through further study, information can be obtained about spectral properties and dynamics within the inhomogeneous line that cannot be obtained using other techniques. The fact that small, persistent, localized changes can be made in inhomogeneously broadened lines at will in these materials is a novel process that deserves continued attention in the research community, for scientific reasons as well as for frequency domain optical storage applications.

III. General Requirements for Frequency Domain Optical Storage

We turn now to a discussion of the frequency domain optical storage concept in slightly more detail, in order to understand what requirements are placed on the materials and the engineering design by this possible future application. In part B of this section, research efforts to demonstrate the principal engineering requirements will be summarized, and part C will conclude this section with an overview of research aimed at demonstrating the most important materials requirements.

A. Basic Arrangement of a Frequency Domain Optical Store

Figure 5 illustrates one way to organize a frequency domain optical store. Starting at the top of the figure, a sequence of "1's" and "0's" has been burned into an inhomogeneously

broadened line within one laser focal volume. (We assume for definiteness that 1000 bits can be written in the frequency domain, although this number may vary depending upon the material.) Furthermore, 10 μm diameter laser spots are assumed, because maintaining 1 μm diameter focused spots over a large field of view would be expensive and impractical. (This is not a serious drawback, because areal densities larger than 10^9 bits/cm² provide no particular advantage. The real challenge when large areal densities are concerned is to access the various bits at the highest possible rate with the lowest cost, because in this regime the total cost of a storage system is dominated by the cost of the actuators. PHB meets this challenge, as will be described presently.)

On one "chip" in the storage system, any one of a large number of laser spots could be accessed in the x-y plane using galvanometer beam deflection. Sixteen to 64 chips might be arranged in a rectangular pattern to form one arm of the storage system, which would contain from 2-8 gigabytes of storage. All of the chips in the arm might be accessed in parallel, using a bundle of laser beams. Of particular importance is the fact that moving the bundle of beams to a particular spot on each of the chips in the arm can be done using a simple mirror mounted on a galvanometer. Galvo access features fast (2 ms) access times, which is 10-20 times faster than access via voice coils and rotation of the recording medium. One possible limitation of galvo access is that only a 1000x1000 spot angular range can be accessed with a single pair of x-y galvos. This is where the additional dimension produces a big advantage: with PHB, $1000 \times 1000 \times 1000 = 10^9$ bits can be accessed with one x-y galvo pair and tuning of the laser frequency. Without PHB, only 10^6 bits can be accessed by each x-y galvo pair and consequently, a galvo-accessed, 1 bit per spot storage system would require too many actuators.

The recording materials would be immersed in a bath of liquid helium. This is essential to keep the absorption line inhomogeneously broadened. Even "zero-phonon" lines broaden with temperature due to phonon scattering effects, and at elevated temperatures the homogeneous width can easily be larger than the inhomogeneous width. Furthermore, for most materials the pattern of spectral holes erases if the material warms up above a critical temperature depending on the material. This may be due to two effects: reversal of the photoinduced change leading to hole formation, or relaxation of the strain distribution that defines the inhomogeneous line. For this reason, the cryostat design should be understandably conservative. Large-volume cryostats are available today that have boil-off times of a week or even a month in the absence of all electrical power. (Of course, the need for a conservative cryostat design makes a frequency domain optical storage system practical only for fairly large databases.) Alternatively, as will be described below, some materials have the novel property of retaining the pattern of spectral holes after cycling to room temperature. If these materials can be used in an actual system, the need for a conservative cryostat is not so large. Low temperatures will still be necessary for reading and writing of the spectral holes, however.

Finally, the reading and writing laser should be a semiconductor diode laser, because these devices are small, reliable, inexpensive, single mode, and current tunable. At present, GaAlAs diode lasers operating in the range 8000-8500 Å have received the most development, but diode lasers in nearby wavelength ranges are beginning to be commercially available. Of particular importance is the fact that the lasers and other central components would be located outside the liquid helium environment. The reading and writing laser beam could be brought into and out of the liquid helium bath through cryostat windows or fiber optics. This has the distinct advantage of keeping the number of critical elements in a low temperature environment down to a minimum. A bundle of laser beams could be directed as a unit to one

arm of the system, which contains the x-y galvo for accessing particular spatial locations. The laser would be repetitively ramped, say every 30 μ s, over the inhomogeneously broadened line in a sawtooth fashion. This ramping of the laser frequency forms a clock. For writing, the laser power might be increased at those instants of time at which holes are to be burned. For reading, the laser power would be attenuated and the transmitted laser beam would be directed via fiber optics outside of the cryostat to a detector. The readout process then becomes an exercise in laser spectroscopy.

This frequency domain optical storage system features fast random access (due to use of galvanometers) and high data rates (due to the possibility for simultaneous readout by several beams in parallel) as well as high areal density. If proper materials can be found, one would expect such a storage system to be competitive.

B. Engineering Requirements

The general storage system just outlined obviously places a variety of demands on the engineering of the system and on the recording material itself. Table 2 lists some of these engineering and materials requirements along with the experiments and materials in which these properties have been demonstrated in recent research. It is important to realize that the goal of most of what has been done up to the present has been to establish proofs of principle, i. e., to observe a required property in any material without requiring that the material satisfy the complete set of required properties. The principal engineering requirements will be described first, and then the materials requirements will be presented in ever-increasing detail.

Hole detection is a crucial requirement, in that holes must be detected in a time on the order of 30 ns/bit (30 μ s laser scan divided by 1000 bits in the frequency domain) with

signal-to-noise ratio adequate for digital data retrieval. Here a variety of techniques for detecting spectral holes will only be mentioned, and the reader is urged to consult the references for more detail. Laser FM spectroscopy [64] [65] is a zero-background method that involves phase modulating the incident laser beam at a fixed rf frequency and using the spectral holes to convert the phase modulation into amplitude modulation at the rf frequency. The technique can detect a hole in a time on the order of the rf period, which would be near 10 ns for a 100 MHz rf frequency. Although the method has been demonstrated to be shot-noise-limited under double modulation conditions[66], only recently has shot-noise-limited performance and removal of residual amplitude modulation been realized without secondary modulation of the absorption [67] [68] . HUMPH (for High Resolution Ultrasonic Modulation of Persistent Holes) is an internal modulation technique that also shows promise [69] [70] . In this technique, an ultrasonic field generates a time-varying strain field that modulates the shape of the spectral hole. FREMPLOSPECT (for Frequency Modulated Polarization Spectroscopy) [71] [72] utilizes the dichroism and birefringence of spectral holes for sensitive, zero background detection of polarization-anisotropic spectral features. Wavelength modulation of diode lasers has also been utilized for zero background sensitive detection [73] [74] . Time-domain readout methods [75] [76] [77] and holographic readout methods [78] have also been demonstrated. On the whole, the problem of detection of spectral holes is fairly well in hand, given the large number of techniques available. It still remains to be demonstrated that shot-noise-limited detection with adequate signal-to-noise can be performed with diode lasers in 10 μ m diameter spots, and experiments to address this problem are in progress.

Continuing in Table 2 with engineering requirements for frequency domain optical storage, x-y access could reasonably be achieved with galvanometer beam deflection, and access in the

frequency domain would be achieved simply by current and/or temperature tuning of the diode laser. One further problem of interest is the need to focus to a particular 10 μm diameter spot and servo control the galvanometer so as to maintain the laser beam on the selected storage location. A servo scheme using a Ronchi grating on the recording medium with dithering of the galvanometer mirror has been demonstrated in liquid helium[79]. Demonstrations of negligible crosstalk between data stored in adjacent 10 μm spots has been demonstrated using as a recording material R' color centers in LiF [80] [81] [82] .

One may conclude that the engineering issues for frequency domain optical storage are solvable within the current state of the art, although single-mode diode lasers with wider tuning ranges would be desirable. The final problem of detecting a hole in 30 ns with high signal-to-noise with a 10 μm laser spot still remains, and this problem depends heavily on the nature of the photochemical process occurring in the recording material, as will be described below.

C. General Materials Requirements

Any reasonable system design also places demands on the properties of the photoactive hole-burning material, and the second part of Table 2 lists some of these requirements. For example, the hole widths at liquid helium temperatures should be in the range 100-500 MHz. Holes should not be much narrower, or power broadening will occur during readout due to low saturation intensities. If the holes are much broader, frequency space will be wasted and excessive demands will be placed on the tuning range of the diode laser. A variety of systems as shown in the Table have yielded hole widths in this range [12] [20] . Of particular interest several years ago was whether or not narrow holes could be burned for organic molecules in

polymer hosts, where the inhomogeneous broadening is extremely large. In recent measurements, hole widths of 120 MHz FWHM have been observed for H₂-phthalocyanine (Pc) in poly(ethylene) (PE) matrices at 1.4 K [12], and even narrower holes have been observed for free-base porphine (H₂P) in PE at 0.3 K [18]. Since the inhomogeneous line is near 100 cm⁻¹ wide for H₂-Pc-PE, the ratio of inhomogeneous to homogeneous widths is on the order of 10⁴ in this system.

As has been stated before, the ultimate PHB mechanism must be active at GaAlAs laser wavelengths (8000-8500 Å). In the early years of PHB research, concern was raised about finding photochemical processes that were operative at this fairly low energy. To address this concern, a proof-of-principle was found in the R' aggregate color center in LiF [22] using an infrared dye laser, and hole writing and reading were quickly demonstrated with a GaAlAs laser [73] as well. Recently, hole-burning at GaAlAs laser wavelengths was also demonstrated for an organic material composed of protonated free-base Pc in a sulfuric acid glass matrix [83].

The problem of reversal of the hole-process is very important because an archival, write-once low temperature storage system would not be very practical. Reversibility occurs to a greater or lesser degree in almost all materials, with the exception of complete decomposition reactions that occur for s-tetrazine and dimethyl-s-tetrazine [28]. The proton tautomerization systems (H₂P and H₂Pc) offer a good example of what is desired: the educt and product are simply related and have localized excitations so that one may be transformed into the other and vice-versa [6] [14] [16]. Materials that photoionize also show reversibility; for example, color center PHB can be reversed by irradiation at high energies to release electrons from traps [20]. Rather than trapping the electrons at unknown sites in the host, a

better mechanism would be to have a donor-acceptor pair close to one another so that the electron could be shuffled back and forth indefinitely. Studies to determine the number of erase cycles and to optimize materials for reversibility are areas deserving further research.

Long hole lifetimes at low temperatures is an important requirement for data storage applications. Most of the materials mentioned in this article have hole lifetimes at least on the order of days, limited so far only by the persistence of the experimenter to maintain a cryostat at liquid helium temperatures for weeks or more. One careful study of hole lifetimes has been performed for the case of quinizarin in glasses[32], and half-lives on the order of 20,000 years are estimated for the deuterated system.

One critical proof-of-principle, burning of detectable holes in times on the order of 30 ns, has only recently been completed. Prior to late 1983, no detectable holes had been burned in times less than 1 ms, and nanosecond burning times are obviously required for a large data storage system. For the case of H_2Pc in poly(ethylene), hole-burning at constant energy yielded smaller and smaller holes as the burning time was decreased, due to a bottleneck in the hole-burning process[12], the triplet decay time to the singlet ground state. Using a variation of FM spectroscopy to probe the sample with extremely low reading power levels, detectable holes were burned in less than 100 ns for tetra-*t*-butyl- H_2Pc in PE [13]. The basic problem that surfaced as a result of this study was the realization that for any system, a bottleneck exists in the burning process defined by the excited state lifetime, which should be on the order of 10 ns[84]. Since holes must be burned in 30 ns or so, a given center can at most absorb only a few photons during the typical burning time. Since quantum efficiencies for PHB are usually less than 1% to as small as 10^{-7} , the holes that are burned in short times are necessarily very shallow. To detect shallow holes, high reading powers are required to increase the

signal-to-noise, but high reading powers destroy the written information by causing photochemistry over the entire laser scan range. This is why an extremely sensitive detection method with very low reading power was required to detect the holes burned in 100 ns.

The last three entries in Table 2 address this problem in detail, and we defer discussion of these points to the next two sections. To summarize, the existence of most of the required properties has been separately demonstrated in a number of inorganic and organic systems, which attests to the high rate of recent progress in PHB research.

IV. Single Photon Recording Mechanisms

Let us now focus on the entry in the table that is third from the bottom: a material in order to be useful in a practical storage system must simultaneously show all the required properties: the ability to form deep holes in short burning times and yet allow fast reading at high signal-to-noise ratios with focused beams. For example, a material with low hole-burning efficiency would be quite easy to read without serious destruction of the written holes, but such a system would be difficult to write with high contrast in short burning times. Conversely, a system that shows fast burning due to a high quantum efficiency for hole production would be difficult to read without burning of the unwritten centers by the tightly focused reading beam (See Section III. C. above).

To understand this problem more fully, a thorough analysis of the coupled reading-writing problem in small spots for materials with single-photon or monophotonic hole-burning mechanisms has been recently completed[85]. The essential problem with single-photon processes is that there is no threshold in the hole formation mechanism. The process of hole

detection requires the absorption of photons by the remaining unburned centers, and if high powers are necessary to detect the dip in the absorption line with adequate signal-to-noise, the hole pattern will be destroyed. This problem was analyzed in detail to determine whether any combination of single-photon materials parameters would yield acceptable reading performance.

Figure 7 shows the general level scheme for single-photon mechanisms. A photon flux F is incident on a general center with a cross section for absorption σ . The center may then either decay back to the original ground state with rate Γ_1 , or it may convert with probability (or quantum efficiency [33]) η to a new ground state, forming a spectral hole. The basic plan is to burn the deepest hole that can be burned in 30 ns and then read in 30 ns and require that the signal-to-noise ratio be large enough for practical digital data retrieval. Figure 8 shows the results of this optimization problem (the reader is referred to reference [85] for details). A material with specific values of η and σ would be represented by a point on the η - σ plane shown in the figure. Furthermore, since the analysis requires that the absorption coefficient α_0 of the sample be fixed at a constant value that optimizes the signal-to-noise ratio, the concentration of centers necessary to keep α_0 fixed (top axis) must decrease as the cross section increases. In other words, for given η and σ , the concentration listed on the top axis must be achieved in order to optimize signal-to-noise ratio. The triangular region represents the class of materials that would yield acceptable signal-to-noise ratios for the first read after burning a single hole. This means that a useful single-photon material must have low absorption cross section and high quantum efficiency, with sufficient solubility in the host to yield the concentrations shown on the upper axis of the figure. The various symbols on the figure locate a representative class of previously studied single-photon materials, none of which fall within the allowed region. This is mostly due to coincidence - since early

investigators were unaware of the need to consider low cross section materials, only easily studied high cross section materials were considered.

The results in Figure 8 show that a new challenge exists for workers in the field of PHB: find single-photon materials that have values of quantum efficiency and cross section that fall within the allowed region, as well as solubilities that allow concentrations shown along the top axis. One might look for hole-burning in partially allowed transitions, such as $n-\pi^*$ transitions of organic molecules and d-f transitions of divalent rare earth systems.

Figure 9 contains an enlargement of the allowed region where the number of reads that can be achieved for each η - σ pair has been shown as contours of constant numbers of reads. Near the boundary line and in the upper right portion of the allowed triangle, the number of reads is fairly small, and a practical storage system based on such materials would require excessive refreshing capability. For materials in the upper left region with η near 0.1 and σ near 10^{-15} cm², thousands to tens of thousands of reads can be achieved before refresh is required. It is reasonable to assume that the refresh function would be implemented in the following fashion. The data would be stored with error-correcting codes as is standard in the data storage industry today. When an error is detected from data stored in a given spot, the actual data would be reconstructed from the error-correcting code, and all the bits in that spot would then be erased and re-written. It is a matter of debate and engineering trade-offs at which values of M^* this refresh requirement would become impractical, but we assume that with M^* greater than 1000, the overhead from the refresh capability would not be excessive.

One consideration not mentioned so far is the actual power required to detect the spectral holes. The analysis in Reference [85] shows that the power requirements are well within current and near-term projected power levels available from diode lasers. The related question

of sample heating is complex, and the amount by which a sample warms in superfluid helium depends upon the low temperature thermal conductivity, heat capacity and Kapitza resistance of the sample in question. Preliminary modeling studies [86] indicate that sample heating effects are tolerable for crystalline hosts; however, for polymeric hosts measurements of sample heating must be performed for each individual case.

Another consideration not mentioned so far is the number of centers required to store a single bit of information. A little reflection will convince the reader that the number of centers per bit should not be too small, otherwise statistical fluctuations in the number of centers representing one bit will introduce excessive noise and increase the bit error rate. In particular, the situation corresponding to one center or molecule per bit is definitely not desirable. For the "ideal" single photon system in the upper left hand corner of Figure 9, greater than 10^{10} centers store each bit. If the fluctuations in the number of burned centers were Poisson-distributed, the error introduced by 10^{10} centers per bit would only be 1 part in 10^5 .

It may be concluded that single-photon materials with $\eta\text{-}\sigma$ values in the upper left-hand corner of Figure 9 might be practical materials for frequency domain optical storage. Such materials should have efficiencies near 0.1 and oscillator strengths in the range 10^{-4} to 10^{-5} . (For 100 MHz homogeneous widths, the oscillator strength is equal to 1 for $\sigma = 1.7 \times 10^{-10}$ cm².) However, no single-photon materials have been studied to date that lie even within the allowed region for the first read shown in Figure 8. This work thus provides future research with a clear direction as to which single-photon PHB materials should be investigated for frequency domain optical storage applications.

V. Gated, 2-step Recording Mechanisms

The parameter space of useful η - σ values for single-photon mechanisms is somewhat small compared to the entire range of these two materials parameters. Consequently, it is of paramount importance in future studies to consider those materials that do not suffer from the intrinsic limitations of single-photon, monophotonic processes with no threshold. One such class of materials are those with two-step PHB mechanisms, called gated mechanisms in the second to the last entry in Table 2. Figure 10 shows the general idea of gating. The wavelength λ_1 excites a homogeneous packet within an inhomogeneously broadened line. If no external field is present, the center returns to the original ground state without forming a spectral hole. However, in the presence of λ_1 and some external field, the center undergoes the transformation leading to hole-burning. This is the origin of the term "gating": the external field acts as a gate on the hole-burning process. The hole may be detected using λ_1 alone, since hole detection is merely probing the ground state distribution of those centers that did not react to form the spectral hole. Since the external field is not present during the reading process, hole detection may then be nondestructive. In effect, gated mechanisms add a much-needed "threshold" to the writing process. The external field may be a second photon of a different wavelength or the gating could perhaps be achieved by any other external field, such as electric field, magnetic field, stress field, and the like.

Recent research at IBM has been devoted to a search for gated or two-color or photon-gated PHB mechanisms [87] in inorganic as well as organic materials. In this case, two photons (of different wavelengths) are required for the photoinduced change leading to hole-burning (writing). In recent experiments, photon gated PHB has been observed for the first time for Sm^{+2} ions in BaClF crystals[88]. The mechanism is thought to be that shown

schematically in Figure 11. The first wavelength, λ_1 , is near 690 nm and excites the system from a 7F_0 ground state (level 1) to a 5D_0 level (level 2). Extended irradiation at 690 nm produces essentially no hole production, but brief periods of simultaneous irradiation with $\lambda_2=514$ nm allows deep holes to be burned at λ_1 . The second photon excites the ion from 5D_0 to the conduction band or to an autoionizing level and the photoejected electron is subsequently trapped in the host matrix. The gating ratio, or the ratio of single-photon hole production to gated hole production, has been observed to be greater than 10^4 in preliminary experiments[88].

This material has a further exciting and unexpected property: a pattern of holes burned at low temperature persists even after cycling up to room temperature and back down to liquid helium temperatures. Apparently, the electrons are trapped at sites with very high barriers, and the relaxation of strains upon cycling is small enough to prevent loss of the site selection. This discovery shows that materials exist that can relieve one of the most serious concerns with frequency domain optical storage: volatility of the stored data. Further experiments are in progress to understand this novel process, and the reader is urged to consult the references for more detail[88].

Moreover, two-color photon gated PHB has also been recently observed in an organic material composed of carbazole molecules in boric acid glasses[89]. The presumed mechanism for this material is outlined in Figure 12. Upon excitation in the singlet-singlet origin with $\lambda_1=335$ nm, the molecule undergoes intersystem crossing with a high yield to form triplets. From T_1 , the molecules return to the original ground state if λ_2 is not present, and no hole is formed. However, in the presence of $\lambda_2=360-405$ nm, holes are formed at the singlet excitation wavelength, λ_1 , presumably due to photoionization of the molecule in the triplet

manifold and trapping of the ejected electron in the boric acid glass matrix. The observation of gating in an organic system now allows the full power of organic synthetic techniques to be used in the process of materials optimization. These two new examples of gated spectral hole-burning have opened up a new class of materials for PHB, and considering the limitations on single-photon materials, the search for gated mechanisms should be an important area for future study.

VI. Conclusion

This article has presented a summary of the basic PHB process, research to understand PHB mechanisms in photochemical as well as nonphotochemical processes, and engineering and materials requirements that are imposed by the general structure of a frequency domain optical storage system. In addition, a general analysis of single-photon mechanisms has underscored the importance of finding gated, 2-step mechanisms for PHB. Recent discoveries of gated PHB in inorganic and organic systems show that these mechanisms do exist. The way is now opened for an interdisciplinary attack on a new challenge: find and study of gated mechanisms in the detail necessary to yield materials that will satisfy all the requirements for this most interesting application of molecular electronics, frequency domain optical storage.

ACKNOWLEDGEMENTS

The author acknowledges useful and stimulating collaborations over the past three years with G. C. Bjorklund, M. D. Levenson, R. M. Macfarlane, R. M. Shelby, and J. D. Swalen on many of the results reported in this article. The author thanks D. Haarer for permission to reprint Figures 3-5 from reference [5]. The research at IBM has been supported in part by the Office of Naval Research.

TABLE 1: MATERIALS EXHIBITING PERSISTENT SPECTRAL HOLE-BURNING

Material	Mechanism	Reference
<i>Photochemical</i>		
Free-base phthalocyanine in n-alkanes, polymers	Proton tautomerization	5-7,10-13
Free-base porphyrins and chlorin in n-alkanes, polymers	Proton tautomerization	14-19
Color Centers: F_3^+ in NaF, R' in LiF, centers in diamond, ...	Electron transfer, trapping	20-26
Trapped electrons in organic glasses	Photoionization	27
Quinizarin in glasses	H-bond rearrangements	5,7,28-33
s-tetrazine, dimethyl-s-tetrazine in crystals and polymers	Decomposition	28,34-37
Divalent rare earth ions in crystals	Photoionization	38,39
1,2-difluoroethane in rare gas matrices	Conformer interconversion	40-42
<i>Photophysical (nonphotochemical)</i>		
Electronic transitions of molecules in glasses and polymers (tetracene, perylene, resorufin, rigid dye molecules, ...)	Host TLS transitions	8,43-48
Ions in glasses and polymers	Rearrangement of local host structure	49-52
Pentacene, thioindigo in hydrogen-bonded organic crystals	Host H-bond rearrangements	53-55
ReO_4^- , CN^- in alkali halides	Center reorientation	9,56-58
Trivalent rare earths in crystals	Optical pumping in nuclear hyperfine and quadrupole levels	59-63

TABLE 2: ENGINEERING AND MATERIAL REQUIREMENTS FOR FREQUENCY DOMAIN OPTICAL STORAGE

Property	Material or Technique	Reference
<i>Engineering Requirements</i>		
Hole detection (30 ns/bit, high SNR)	FM, HUMPH, FREMPOLSPECT, ...	64-78
x-y access	Galvanometer beam deflection	-
Access in frequency space	Current and temperature tuning	73,74
Focus/servo in liquid He	Ronchi grating, dither	79
No crosstalk between adjacent spots	Measured: R' in LiF	80-82
<i>Material Requirements</i>		
$\Delta\nu_{hole} = 100 - 500MHz$	color centers, H ₂ Pc-PE,...	12,20
GaAlAs compatibility	R' in LiF(8330 Å), H ₂ Pc-H ₂ SO ₄ , ...	22,73,83
Reversible burning	H ₂ Pc, H ₂ P, color centers, ...	6,14,16, 20
Long hole lifetime at low temperatures	Quinizarin in glasses	32
Fast burning (30 ns/bit)	(tBu) ₄ -H ₂ Pc-PE	13
Fast burning, high SNR, fast reading, focused spot	Difficult for single-photon processes	85
Gated hole-burning mechanism	Sm ²⁺ in BaClF, carbazole in boric acid	88,89
Room temperature cycling	Sm ²⁺ in BaClF	88

REFERENCES

- [1] See for example A. E. Bell, Laser Focus/Electro-Optics 19, 61 (August 1983) and A. E. Bell, Laser Focus/Electro-Optics 19, 125 (September 1983), and references therein.

- [2] G. Castro, D. Haarer, R. M. Macfarlane, and H. P. Trommsdorff, "Frequency selective optical data storage system," U. S. Patent No. 4,101,976, (1978).

- [3] D. Haarer, Proc. Soc. Photo-Opt. Inst. Engr. 177, 97 (1979).

- [4] G. C. Bjorklund, W. Lenth, and C. Ortiz, Proc. Soc. Photo-Opt. Instr. Eng. 298, 107 (1981).

- [5] A. R. Gutierrez, J. Friedrich, D. Haarer, and H. Wolfrum, IBM J. Res. Devel. 26, 198 (1982), and references therein.

- [6] L. A. Rebane, A. A. Gorokhovskii, and J. V. Kikas, Appl. Phys. B29, 235-250 (1982), and references therein.

- [7] J. Friedrich and D. Haarer, Angew. Chemie 23, 113 (1984), and references therein.

- [8] G. J. Small, in Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, V. M. Agranovitch and R. M. Hochstrasser, editors, (North-Holland, Amsterdam, 1983), pp. 515-554.
- [9] W. E. Moerner, A. R. Chraplyvy, A. J. Sievers, and R. H. Silsbee, Phys. Rev. B 28, 7244 (1983), and references therein.
- [10] A. A. Gorokhovskii, R. K. Kaarli, and L. A. Rebane, JETP Lett. 20, 216 (1974).
- [11] W. Richter, G. Schulte, and D. Haarer, Opt. Commun. 51, 412 (1984).
- [12] W. E. Moerner, in Proceedings of the International Conference: Lasers '83, R. C. Powell, editor, (STS Press, McLean, VA, 1983), p. 489.
- [13] M. Romagnoli, W. E. Moerner, F. M. Schellenberg, M. D. Levenson, and G. C. Bjorklund, J. Opt. Soc. Am. B: Optical Physics 1, 341 (1984).
- [14] S. Völker and J. H. van der Waals, Molec. Phys. 32, 1703 (1976).
- [15] S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, J. Chem. Phys. 67, 1759 (1977).
- [16] S. Völker and R. M. Macfarlane, IBM J. Res. Devel. 23, 547 (1979).

- [17] S. Völker and R. M. Macfarlane, J. Chem. Phys. 73, 4476 (1980).

- [18] H. P. H. Thijssen, R. E. van den Berg, and S. Völker, Chem. Phys. Lett. 103, 23 (1983).

- [19] F. A. Burkhalter, G. W. Suter, and U. P. Wild, Chem. Phys. Lett. 94, 483 (1983).

- [20] R. M. Macfarlane, R. T. Harley, and R. M. Shelby, Rad. Effects 72, 1 (1983), and references therein.

- [21] R. M. Macfarlane and R. M. Shelby, Phys. Rev. Lett. 42, 788 (1979).

- [22] W. E. Moerner, F. M. Schellenberg, and G. C. Bjorklund, Appl. Phys. B28, 263 (1982);
W. E. Moerner, P. Pokrowsky, F. M. Schellenberg, and G. C. Bjorklund (to be published).

- [23] M. D. Levenson, R. M. Macfarlane, and R. M. Shelby, Phys. Rev. B 22, 4915 (1980).

- [24] R. T. Harley, M. J. Henderson, and R. M. Macfarlane, J. Phys. C: Sol. St. Phys. 17, L233 (1984).

- [25] W. E. Moerner, F. M. Schellenberg, G. C. Bjorklund, P. Kaipa, and F. Lüty, Phys. Rev. B. (in press, 1985).

- [26] C. Ortiz, R. M. Macfarlane, R. M. Shelby, W. Lenth, and G. C. Bjorklund, Appl. Phys. 25, 87 (1981).
- [27] S. L. Hager and J. E. Willard, J. Chem. Phys. 61, 3244 (1974).
- [28] D. M. Burland and D. Haarer, IBM J. Res. Devel. 23, 534 (1979), and references therein.
- [29] F. Drissler, F. Graf, and D. Haarer, J. Chem. Phys. 72, 4996 (1980).
- [30] J. Friedrich, J. D. Swalen, and D. Haarer, J. Chem. Phys. 73, 705 (1980).
- [31] J. Friedrich, H. Wolfrum, and D. Haarer, J. Chem. Phys. 77, 2309 (1982).
- [32] W. Breinl, J. Friedrich, and D. Haarer, Chem. Phys. Lett. 106, 487 (1984).
- [33] W. E. Moerner, M. Gehrtz, and A. L. Huston, J. Phys. Chem. 88, 6459 (1984).
- [34] H. de Vries and D. A. Wiersma, Phys. Rev. Lett. 36, 91 (1976).
- [35] H. de Vries and D. A. Wiersma, Chem. Phys. Lett. 51, 565 (1977).
- [36] R. M. Hochstrasser and D. S. King, J. Am. Chem. Soc. 97, 4760 (1975).
- [37] E. Cuellar and G. Castro, Chem. Phys. 54, 217 (1981).

- [38] R. M. Macfarlane and R. M. Shelby, Opt. Lett. 9, 533 (1984).
- [39] R. M. Macfarlane and R. S. Meltzer, Opt. Commun. 52, 320 (1985).
- [40] M. Dubs and H. H. Günthard, Chem. Phys. Lett. 64, 105 (1979).
- [41] M. Dubs, L. Ermanni, and H. H. Günthard, J. Mol. Spect. 91, 458 (1982).
- [42] P. Felder and H. H. Günthard, Chem. Phys. 85, 1 (1984).
- [43] R. Janowiak and H. Bässler, Chem. Phys. Lett. 101, 274 (1983).
- [44] A. A. Gorokhovskii, Y. V. Kikas, V. V. Pal'm, and L. A. Rebane, Sov. Phys. Sol. St. 23, 602 (1981).
- [45] B. M. Kharlamov, R. I. Personov, and L. A. Bykovskaya, Opt. Commun. 12, 191 (1974).
- [46] U. Bogner, P. Schätz, R. Seel, and M. Maier, Chem. Phys. Lett. 102, 267 (1983).
- [47] A. P. Marchetti, M. Scozzafava, and R. H. Young, Chem. Phys. Lett. 51, 424 (1977).
- [48] T. P. Carter, B. L. Fearey, J. M. Hayes, and G. J. Small, Chem. Phys. Lett. 102, 272 (1983).

- [49] R. M. Macfarlane and R. M. Shelby, Opt. Commun. 45, 46 (1983).
- [50] R. M. Macfarlane and R. M. Shelby, in Proceedings of the NATO Advanced Research Workshop on Coherence and Energy Transfer in Glasses, (Plenum, New York, 1984).
- [51] R. M. Shelby, Opt. Lett. 8, 88 (1983).
- [52] G. J. Small, private communication.
- [53] R. W. Olson, H. W. H. Lee, F. G. Patterson, M. D. Fayer, R. M. Shelby, D. P. Burum, and R. M. Macfarlane, J. Chem. Phys. 77, 2283 (1982).
- [54] H. W. H. Lee, C. A. Walsh, and M. D. Fayer, J. Chem. Phys. (in press).
- [55] J. M. Clemens, R. M. Hochstrasser, and H. P. Trommsdorff, J. Chem. Phys. 80, 1744 (1984).
- [56] W. E. Moerner, A. J. Sievers, R. H. Silsbee, A. R. Chraplyvy, and D. K. Lambert, Phys. Rev. Lett. 49, 398 (1982).
- [57] T. R. Gosnell, A. J. Sievers, and R. H. Silsbee, Phys. Rev. Lett. 52, 303 (1984).
- [58] R. C. Spitzer, W. P. Ambrose, and A. J. Sievers (to be published).

[59] R. M. Macfarlane, R. M. Shelby, A. Z. Genack, and D. A. Weitz, Opt. Lett. 5, 462 (1980).

[60] R. M. Macfarlane and R. M. Shelby, Opt. Lett. 6, 96 (1981).

[61] D. P. Burum, R. M. Shelby, and R. M. Macfarlane, Phys. Rev. B 25, 3009 (1982).

[62] R. M. Shelby, A. C. Tropper, R. T. Harley, and R. M. Macfarlane, Opt. Lett. 8, 304 (1983).

[63] R. M. Macfarlane and R. M. Shelby, Opt. Commun., 39, 169 (1981).

[64] G. C. Bjorklund, Opt. Lett. 5, 15 (1980).

[65] G. C. Bjorklund, M. D. Levenson, W. Lenth, and C. Ortiz, Appl. Phys. B32, 145 (1983),
and references therein.

[66] M. D. Levenson, W. E. Moerner, and D. E. Horne, Opt. Lett. 8, 108 (1983).

[67] M. Gehrtz, W. E. Moerner, and G. C. Bjorklund, submitted to Optics Letters.

[68] M. Gertz, G. C. Bjorklund, and E. A. Whittaker, submitted to J. Opt. Soc. Am. B, and
references therein.

[69] A. L. Huston and W. E. Moerner, J. Opt. Soc. Am. B: Opt. Phys. 1, 349 (1984).

- [70] W. E. Moerner and A. L. Huston, submitted to Opt. Lett.
- [71] M. Romagnoli, M. D. Levenson, and G. C. Bjorklund, Opt. Lett. 8, 635 (1983).
- [72] M. Romagnoli, M. D. Levenson, and G. C. Bjorklund, J. Opt. Soc. Am. B: Opt. Phys. 1, 571 (1984).
- [73] P. Pokrowsky, W. E. Moerner, F. Chu, and G. C. Bjorklund, Opt. Lett. 8, 280 (1983).
- [74] P. Pokrowsky, W. Zapka, F. Chu, and G. C. Bjorklund, Opt. Commun. 44, 175 (1983).
- [75] W. H. Hesselink and D. A. Wiersma, Phys. Rev. Lett. 43, 1991 (1979).
- [76] T. W. Mossberg, Opt. Lett. 7, 77 (1982).
- [77] A. K. Rebane, R. K. Kaarli, and P. M. Saari, JETP Lett. 38, 383 (1983).
- [78] A. Renn, A. J. Meixner, U. P. Wild, and F. A. Burkhalter, Chem. Phys. 93, 157 (1985).
- [79] D. J. Bernays, Proc. SPIE, Vol. 498, 175 (1984).
- [80] F. M. Schellenberg, W. E. Moerner, M. D. Levenson, G. C. Bjorklund, and D. J. Bernays (1984), Conference on Lasers and Electro-optics Technical Digest, June 19-22, 1984, Anaheim, California, paper ThI41.

[81] B. H. Schechtman, G. C. Bjorklund, and W. E. Moerner, IBM Research Report # RJ4128, December 8, 1983.

[82] W. Lenth, F. M. Schellenberg, and G. C. Bjorklund, to be published.

[83] H. W. H. Lee, A. L. Huston, M. Gehrtz, and W. E. Moerner, Chem. Phys. Lett. (in press, 1985).

[84] The excited state lifetime cannot be much shorter, or hole widths will increase above 500 MHz. If the excited state lifetime is much longer, power broadening of the holes will occur at lower reading power levels. See reference [85].

[85] W. E. Moerner and M. D. Levenson, J. Opt. Soc. Amer. B: Optical Physics (in press, 1985).

[86] F. M. Schellenberg, (unpublished).

[87] D. M. Burland, F. Carmona, G. Castro, D. Haarer, and R. M. Macfarlane, IBM Tech. Disc. Bull. 21, 3770 (1979).

[88] A. Winnacker, R. M. Shelby, and R. M. Macfarlane, submitted to Optics Letters.

[89] H. W. H. Lee, M. Gehrtz, E. Marinero, and W. E. Moerner, submitted to J. Chem. Phys.

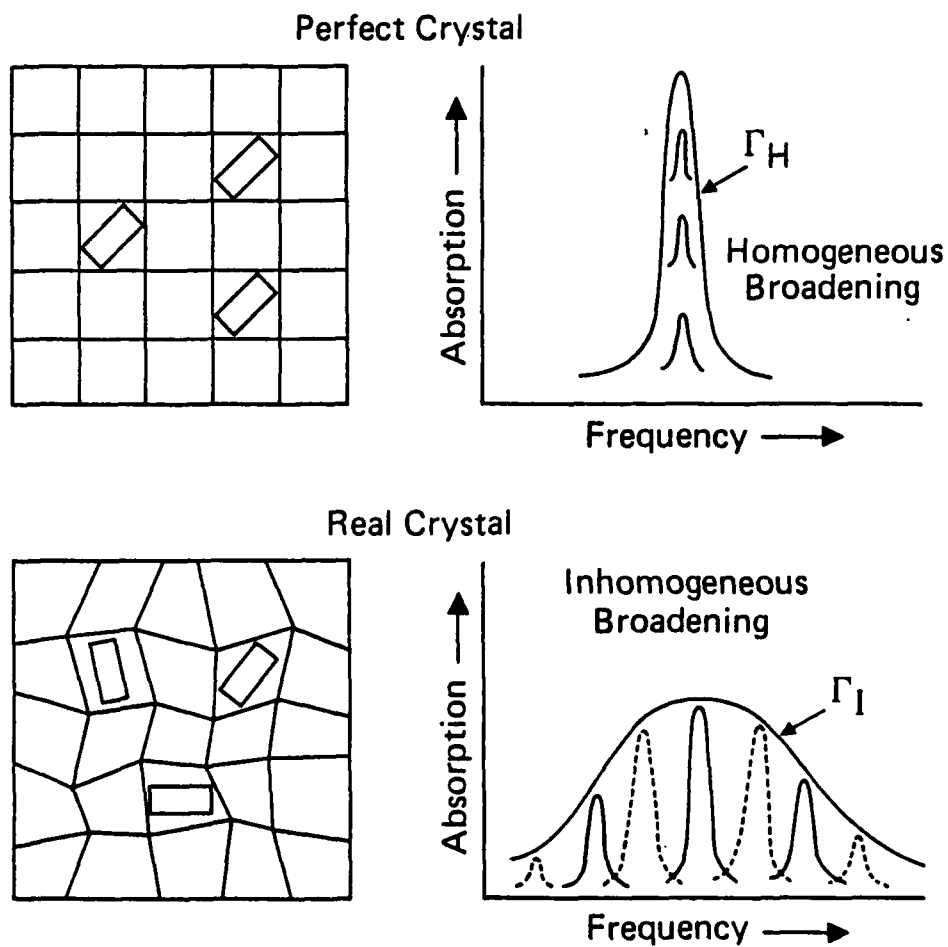


Figure 1. (Upper half) Schematic of absorbers dispersed in a perfect crystal. At low temperatures, the absorption line is homogeneously broadened with width Γ_H . (Lower half) Illustration of one source of inhomogeneous broadening in real solid matrices. The distribution of local environments leads to a distribution of center frequencies of absorption. The resulting lineshape has width Γ_I .

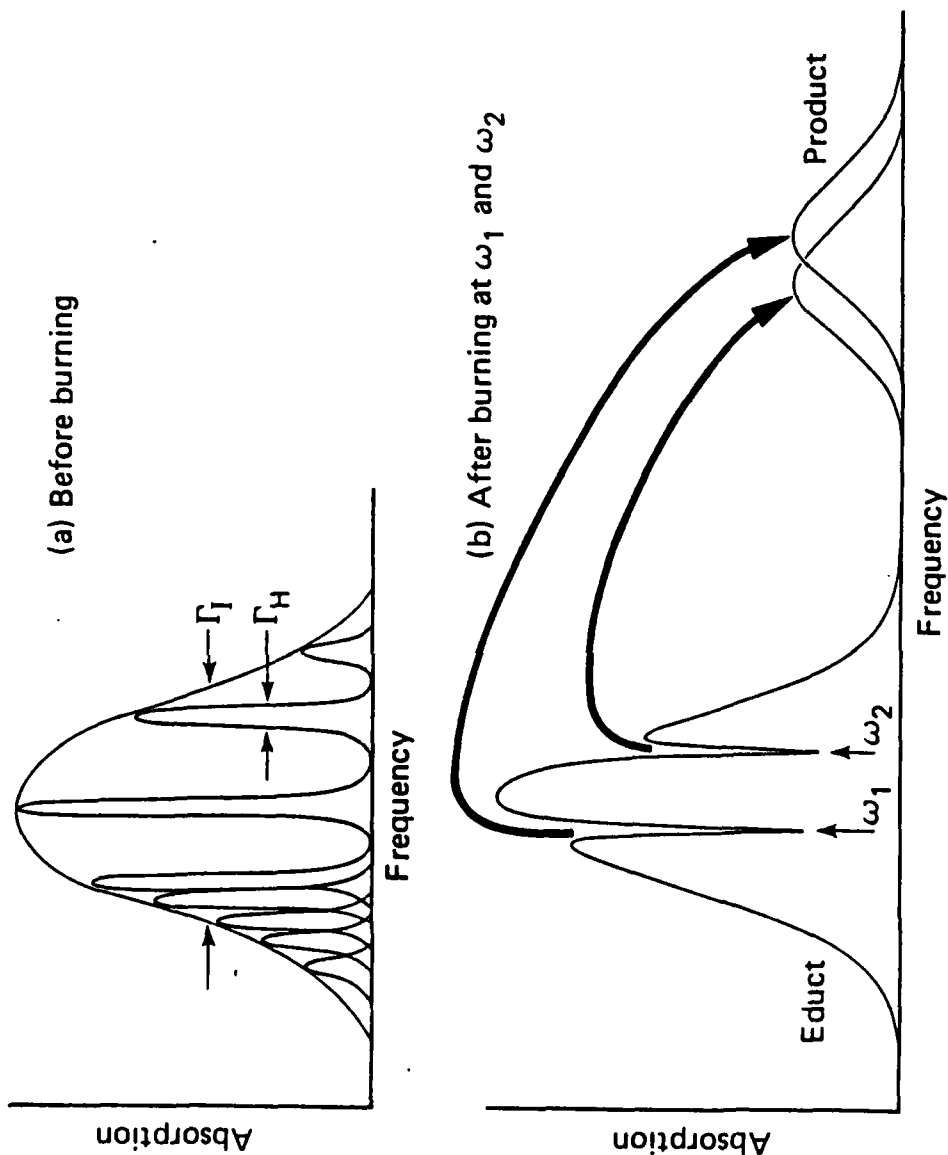


Figure 2. Illustration of the persistent spectral hole formation process. The upper part of the figure shows an inhomogeneously broadened line as described in Figure 1, before any hole-burning has occurred. The lower part of the figure shows how laser irradiation at ω_1 and ω_2 produces a drop in absorption at these frequencies, and a corresponding appearance of product absorption in another region of frequency space.

H₂-phthalocyanine

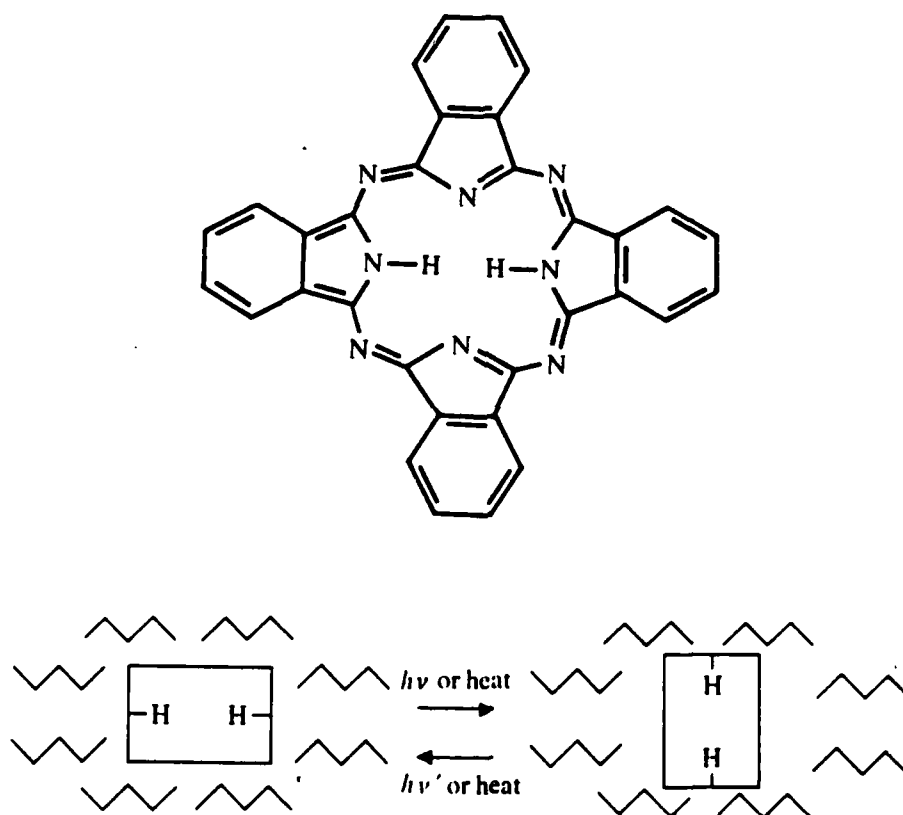


Figure 3. Structure of the free-base phthalocyanine molecule. The two hydrogens in the center can bond to the two nitrogens as shown or to the other two nitrogens in the central cage. In a locally anisotropic host material, the energies of these two forms can be unequal, and the molecule can be transformed between the two tautomers with either light or heat.

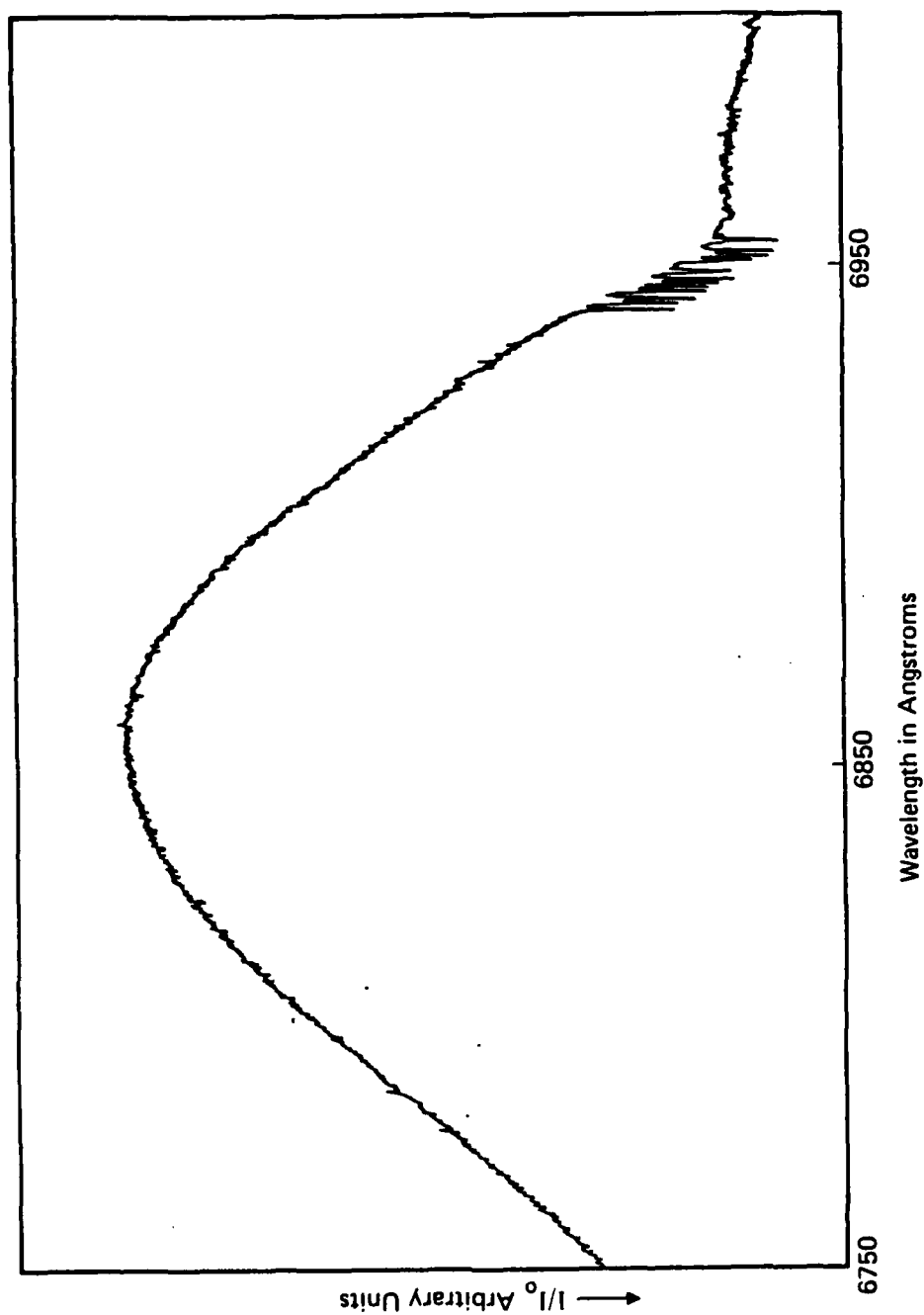


Figure 4. The inhomogeneously broadened 0-0 absorption band of free-base phthalocyanine in PMMA at 4.2K. A sequence of spectral holes has been burned near 6950 Å.

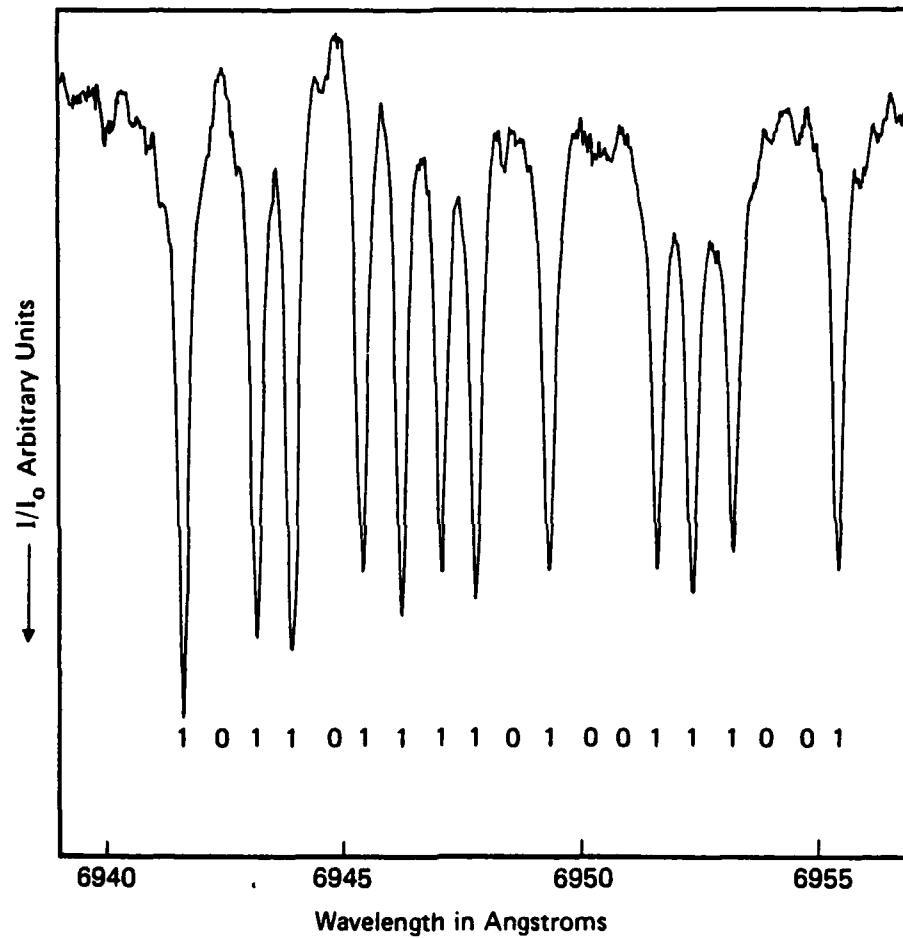


Figure 5. Enlargement of the absorption spectrum of Figure 4 showing twelve spectral holes and a possible decoding of the hole pattern into binary data.

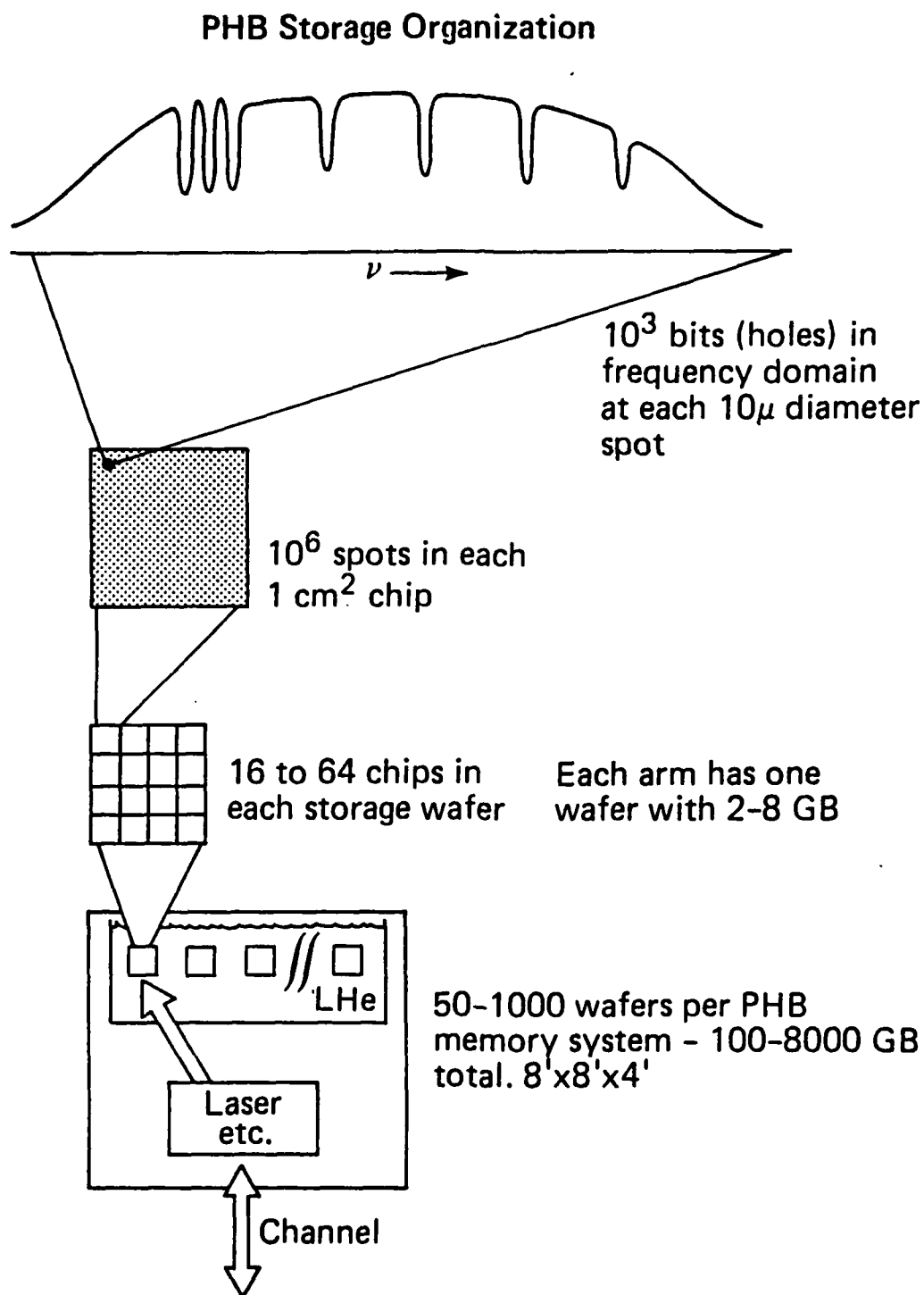


Figure 6. Sketch of the overall organization of a PHB storage system.

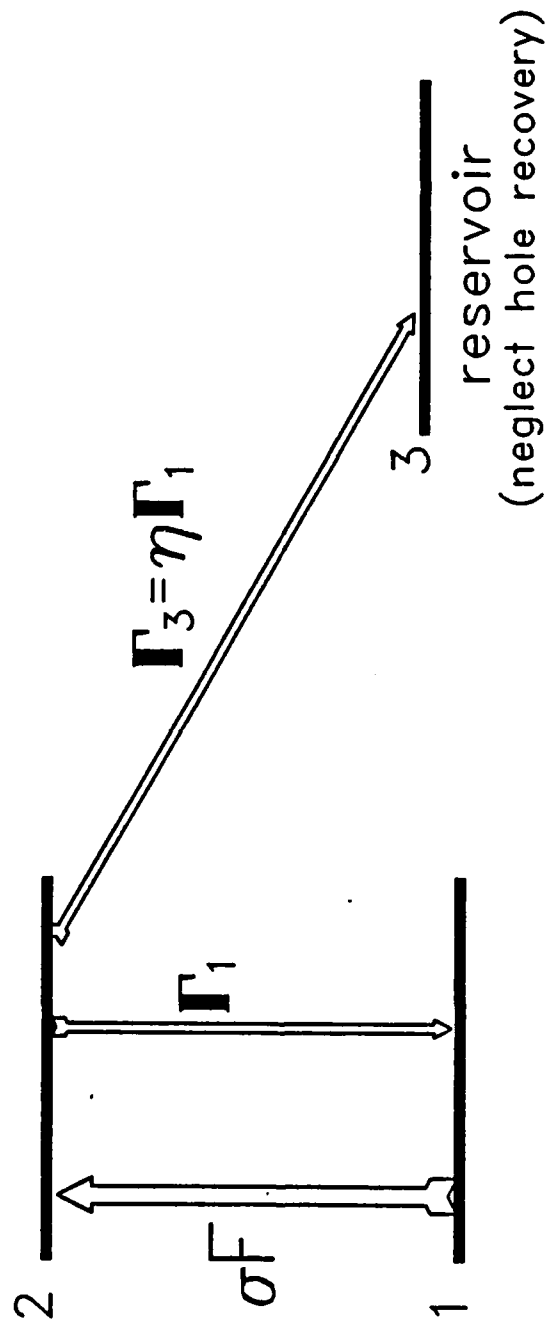


Figure 7. Schematic energy level diagram for absorbing centers with a single-photon hole-burning mechanism. Level 1 is the ground state, level 2 is the excited state, and level 3 is a permanent reservoir ground state that schematically depicts the hole formation process. The various pumping and decay rates are defined in the text.

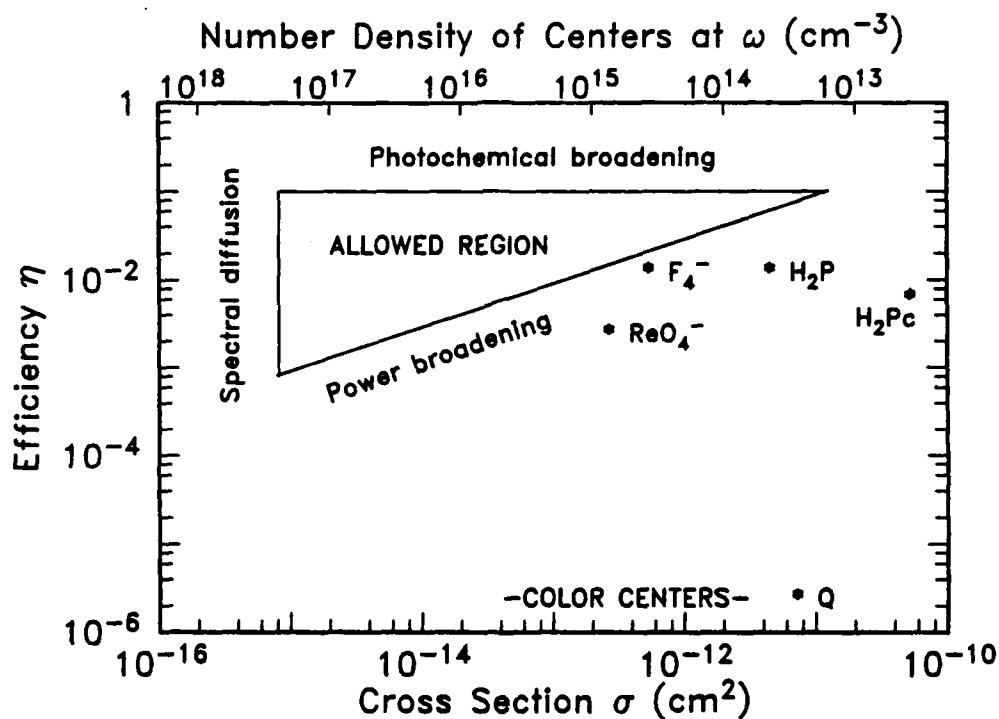


Figure 8. Allowed region of efficiency η , number density of centers at ω , and cross section σ in order for the first read to yield acceptable SNR. The various abbreviations signify: F_4^- - 8892 Å color center in NaF-OH⁻ ([25]); ReO_4^- - perrhenate ion in alkali halides ([9]); H_2P - free-base porphine in n-alkanes ([14]); H_2Pc - free-base phthalocyanine in polymers ([7]); Q - quinizarin in boric acid glass ([33]); and color centers in general ([20]), with the exception of the F_4^- center.

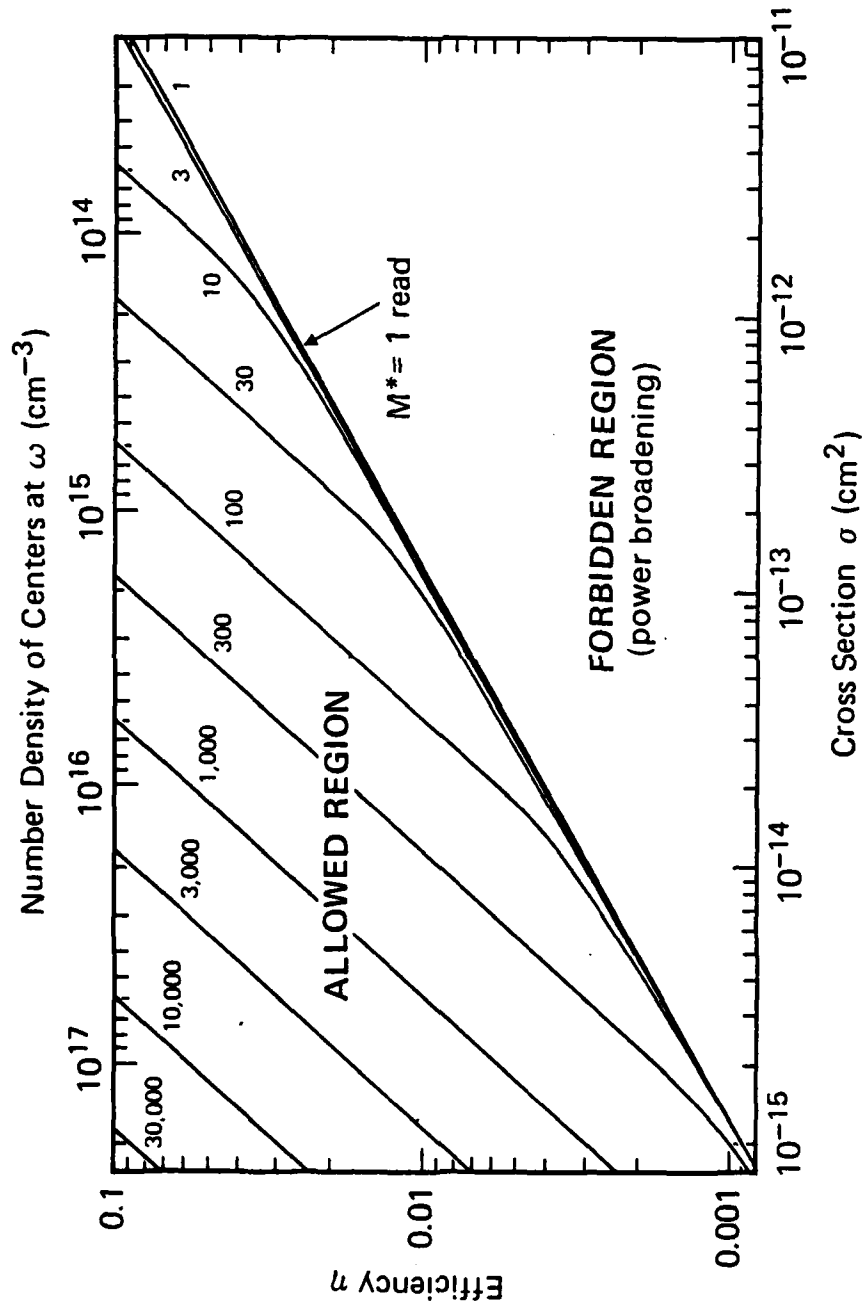


Figure 9. Contour plot in the allowed region of the η - σ plane, showing contours of constant number of reads, M^* . The $M^* = 1$ line is the boundary of the allowed region defined by the constraint of no power broadening during reading. The upper density axis applies only to the case $\alpha_0 L = 2$; i.e., near the $M^* = 1$ line (see reference [85]).

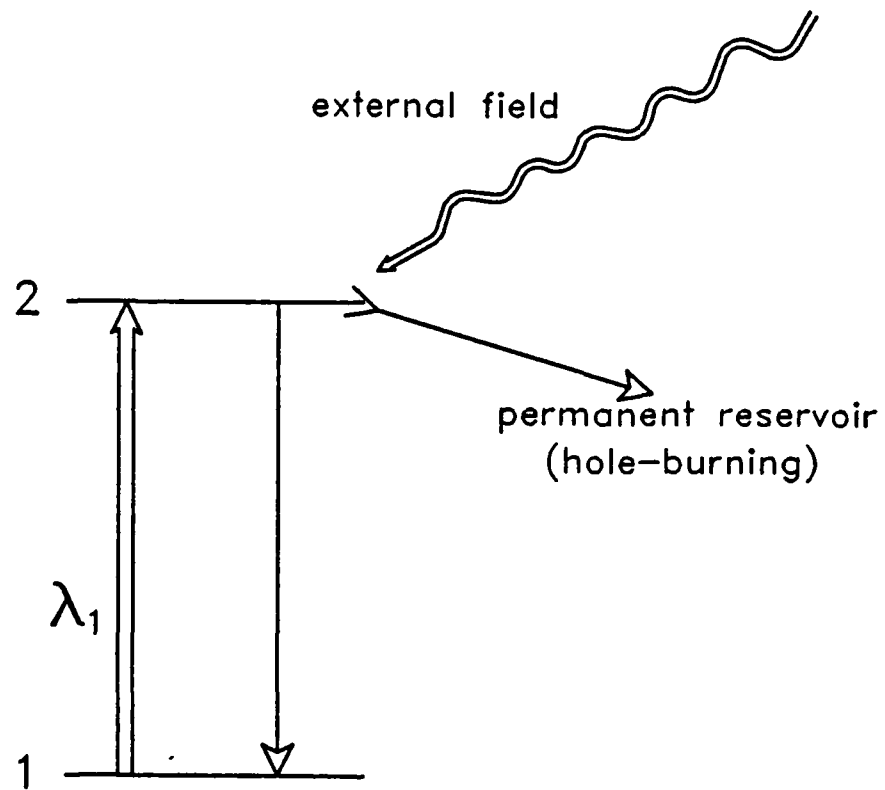


Figure 10. Illustration of basic scheme for gated, two-step PHB.

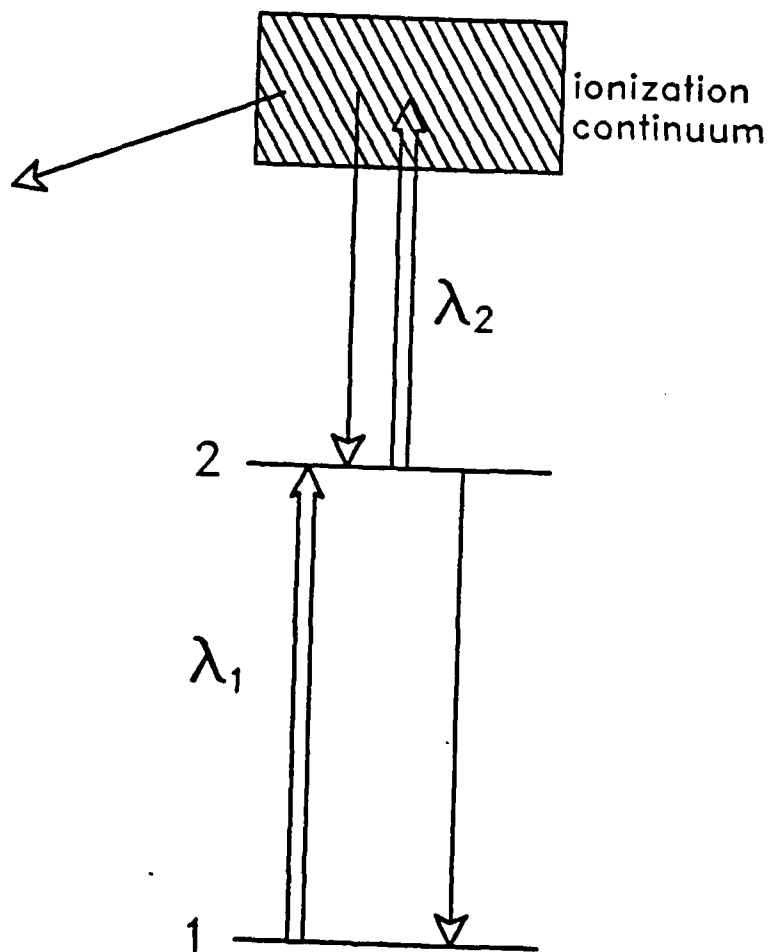


Figure 11. Illustration of gated PHB for a 3-level system.

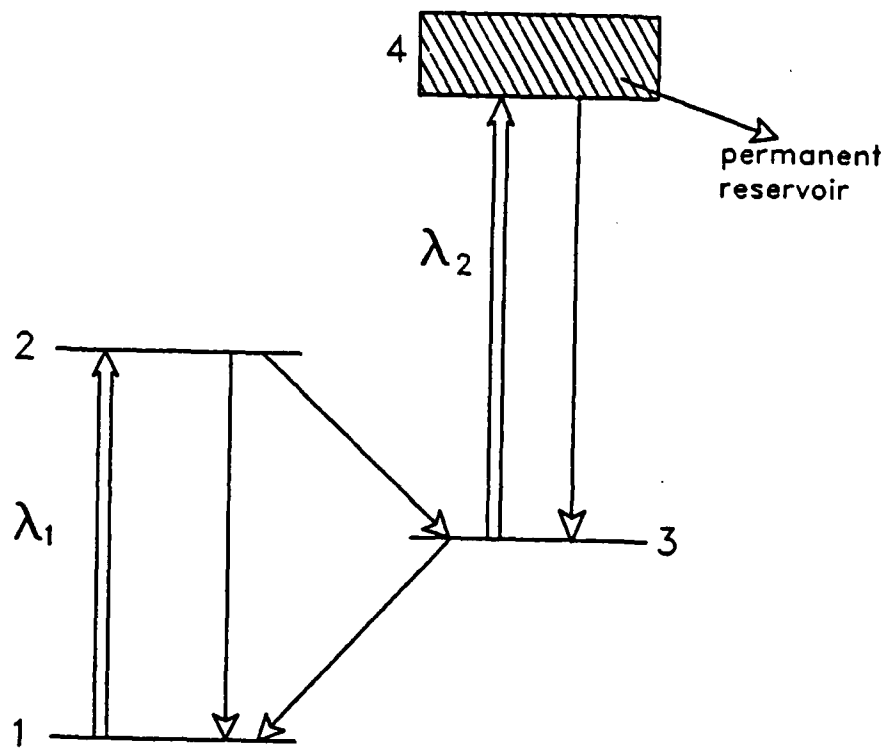


Figure 12. Illustration of gated PHB for a 4-level system.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

12-86

DTIC